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~~CONFORMATION ON ANALYSIS OF POLYMERS~~

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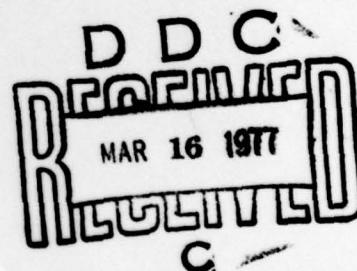
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The project dealt with applying conformational energy calculations to polymers. The early stages involved using energy parameters developed for small or ordinary sized hydrocarbon molecules to calculate the stable conformations and barriers to rotation in isolated hydrocarbon polymer molecules. Later stages involved simulating localized molecular motions postulated to be the basis for relaxations or transitions that control mechanical properties of bulk plastics. Computational methods were developed that permit in favorable circumstances the inclusion of the response of the surrounding chains to localized motions of a chain in the bulk phase. Finally, a new set of energy parameters (or force-field) was developed for phosphazenes so that the conformational energy method can be applied to polyphosphazenes. It should now be possible to study the properties of phosphazene polymers by this method. | | |

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TECHNICAL RESULTS

Many molecular properties of a variety of chemical substances can be calculated or predicted using a technique called conformational energy minimization or "molecular mechanics" as it is sometimes called. The present project dealt with applying conformational energy calculations to polymers. The early stages involved using energy parameters developed for small or ordinary sized hydrocarbon molecules to calculate the stable conformations and barriers to rotation in isolated hydrocarbon polymer molecules.^{3,4,6} Later stages involved simulating localized molecular motions postulated to be the basis for relaxations or transitions that control mechanical properties of bulk plastics. Computational methods were developed that permit in favorable circumstances the inclusion of the response of the surrounding chains to localized motions of a chain in the bulk phase. Finally, a new set of energy parameters (or force-field) was developed for phosphazenes so that the conformational energy method can be applied to that class of compounds. It should now be possible to study the properties of phosphazene polymers by this method.

Some highlights of this work are as follows.

1. Polyisobutylene (butyl rubber) is an elastomeric substance with a low glass temperature. However, molecular models show it to be a **highly** strained molecule that probably would have high barriers to skeletal bond rotation and thus be expected to be kinetically

stiff. We calculated the barriers to rotation and found them to be moderately high.¹ However it was found that considerable localized twisting of the chain can take place without expense of energy and without rotation over a barrier. We proposed that this twisting is sufficient to allow elastomeric behavior and is responsible for the paradoxical behavior of polyisobutylene. This suggestion has since been developed by others.

2. Isotactic polypropylene is a molecule that has steric interferences in all conformations but the 3_1 helix found in the crystal. This has led to speculation that the molecule should find it difficult to coil in solution and would be highly extended in that condition. However experiment shows it to be a rather compact coil in solution. It has been suggested therefore by some that isotactic polypropylene is not really isotactic. In our work² we calculated the magnitude of the steric interferences and showed that the measured solution dimensions are actually in good accord with the calculated conformational properties. Thus there is no need to invoke lack of tacticity to explain the solution properties. This viewpoint has subsequently been accepted by others.

3. Polystyrene is an interesting polymer conformationally because the phenyl group is sterically large but yet is attached to the chain by a bond that is essentially free to rotate. Our calculations show¹⁰ that this freedom of rotation allows the phenyl groups to align themselves cooperatively with chain motions so that they actually do not behave as sterically bulky groups and are effectively smaller than methyl groups. It also was found that because of phenyl flexibility conformational energies were inadequate descriptors and conformational free energies were required. However these could

readily be supplied from our computation technique.

4. Polyethylene and many other polymers show a prominent low temperature mechanical relaxation peak (γ) whose molecular interpretation has inspired much speculation. One explanation is that there are motions of short chain segments that are possible in the glassy matrix of the amorphous fraction. These have been called crankshaft motions. We have modeled crankshaft motions⁵ and found some of the proposed motions are unreasonable but have indentified certain motions that appear to be quite reasonable explanations for the γ processes.

5. One of the problems in modeling molecular motions in bulk polymers is that even though the motions may be localized in a segment of one chain the response of surrounding chains should be included. We have worked out a computational technique that permits this.⁷ We applied it to kink motions in the crystal fraction of polyethylene. In calculating the defect energy of the kink two coordination shells around the kink were allowed to freely deform to accommodate the kink. It is thus becoming possible to model localized motions quite realistically.^{8,9}

6. Polyphosphazenes are an interesting class of polymers that have an inorganic backbone, are elastomers with low glass temperatures when amorphous and have high solvent resistance and thermal stability. When crystalline they have an thermal transition to a crystal that is somehow disordered. The properties of polyphosphazene could profitably be studied by means of conformational energy calculations. In preparation for this we have developed¹¹ the energy parameters or force-field that will allow such calculations. Some exploratory studies of relaxation processes in polyphosphazenes were made by means of the dielectric relaxation method.

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PERSONNEL SUPPORTED AND DEGREES AWARDED

RICHARD H. BOYD, principal investigator

G.E. STEGEN, graduate student. Received M.E. degree, carried out polystyrene calculations.

LAYA KESNER, post-doctoral research associate, participated in developing the force-field for phosphazenes.

C.R. ASHCRAFT, graduate student, Ph.D. awarded for work largely supported by NSF but carried exploratory studies or dielectric relaxation in polyphosphazene.

T. YEMNI, graduate student, Ph.D. awarded for work largely supported by NSF but carried out a dielectric study of the odd-numbered polyamide nylon 77. This polymer is of interest because single crystals are ferroelectric.